

Ab Initio Study of the Formation of $C_3H_3^+$ from the Reaction of CH_3^+ with Acetylene

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Received 28 March 1995; accepted 6 July 1995

ABSTRACT

Ab initio molecular orbital theory has been used to study the mechanism of the formation of $C_3H_3^+$ from the reaction of CH_3^+ with acetylene. The highest level geometry optimizations and frequencies were computed at MP2-FC/6-31G** ; single point energies of all the critical structures were computed to the MP4-FC/6-31G**//MP2-FC/6-31G** theory level. One of the three alternative transition structures leading to the formation of $C_3H_3^+$ gives the cyclopropenyl cation and the other two the propargyl cation. The proportions of $C_3H_2D^+$ and $C_3HD_2^+$ obtained when CD_3^+ reacts with acetylene, and the composite nature of the metastable peak observed for the $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$ fragmentation are explained by assuming a different degree of deuterium scrambling depending on the energy of the system. © 1996 by John Wiley & Sons, Inc.

Introduction

The gas phase reactions of CH_3^+ afford important examples of carbocation chemistry.^{1–8} Ion cyclotron resonance was first used to study the $CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2$ reaction. An overall reaction energy $\Delta H = -59$ kcal/mol and a rate

constant of 1.15×10^9 cm³/s were determined.^{6a} The next experimental studies with a triple quadrupole spectrometer showed that CH_3^+ reacts with acetylene to give $C_3H_3^+$ in very high yield.^{6b} It is likely that $C_3H_3^+$ was the cyclopropenyl cation since when CH_3^+ was replaced by CD_3^+ , $C_3H_2D^+$ and $C_3HD_2^+$ were formed in a 1:2 ratio. A detailed investigation of the collisionally induced fragmentation reactions showed that the composite nature of the metastable peak for

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the $[\text{C}_3\text{H}_5]^+ \rightarrow [\text{C}_3\text{H}_3]^+ + \text{H}_2$ fragmentation results from the cyclopropenyl cation cyclo- C_3H_3^+ (D_{3h}), as well as the allenyl cation $[\text{CH}_2 = \text{C} = \text{CH}]^+$ (C_{2v}).^{6c} Crossed-beam reactions of CH_3^+ with acetylene with a relative collision energy ranging from 0.5 to 2.0 eV gave $\Delta H = -61.1$ kcal/mol for the reaction energy. Participation of a transient C_3H_5^+ complex was implicated, but the clear asymmetry of the distribution indicates that this complex has a very short lifetime. At the lower energies the fraction of the cyclopropenyl cation products are significant, but at higher energies the products are less constrained.^{6d} Measurement of the angular distribution of the ion product velocities and reaction cross sections with 1 to 10 eV relative collision energy confirms that the lifetime of the intermediate complex is only a fraction of the rotational period of the system. With CD_3^+ , the ratio of C_3HD_2^+ and $\text{C}_3\text{H}_2\text{D}^+$ cross sections ranges from 1 in the 10–4 eV collision energy to 1.4 in the 1 eV collision energy. These results were explained by proposing that the reaction between CH_3^+ and acetylene proceeds through two different mechanisms: an insertion mechanism in the high-energy region and an addition mechanism in the low-energy region.^{6e}

We now report an *ab initio* study of the $\text{CH}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}_2$ reaction which leads to a more detailed rationalization of those experimental findings.

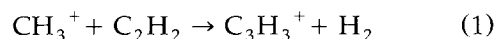
Methods

Ab initio calculations used the Gaussian92 package.⁹ Geometry optimizations at the second order Moeller–Plesset level employed the frozen core approximation¹⁰ and the 6-31G** basis set.¹¹ Harmonic vibrational frequencies, calculated at the same MP2-FC/6-31G** level, characterized stationary points and gave the zero-point vibrational energies (ZPVEs). ZPVEs were scaled by a factor of 0.94.¹² Intrinsic Reaction Coordinate (IRC) calculations starting at the saddle points verified the two minima connected by each transition structure.¹³ MP4(SDTQ)-FC/6-31G**//MP2-FC/6-31G** single points gave our highest level energies.

Results and Discussion

Simulation of the experimental attack of CH_3^+ on acetylene in C_s symmetry [eq. (1)] leads directly

either to the corner-protonated cyclopropene (1 in Figure 1) or to the 2-methylvinyl cation (2 in Figure 1) without encountering any energy barrier. The latter mechanism is complex and involves a hydrogen migration:



Further rearrangement leads to the global C_3H_5^+ minimum—the allyl cation (3 in Figure 1). Besides the three intermediates Structures 1–3 in Figure 1, six transition structures (4–9 in Figure 2) were located and characterized on the C_3H_5^+ potential energy surface. Table I summarizes all the total and relative energies as well as the ZPVEs.

Structure 9 in Figure 2 is the transition structure connecting corner-protonated cyclopropene and the 2-methylvinyl cation. Structure 8 corresponds to the transition state between corner-protonated cyclopropene and the allyl cation. As reported previously,^{8f} the transition structure between the allyl cation and the 2-methylvinyl cation corresponds to an energy barrier of 31.2 kcal/mol at the MP2-

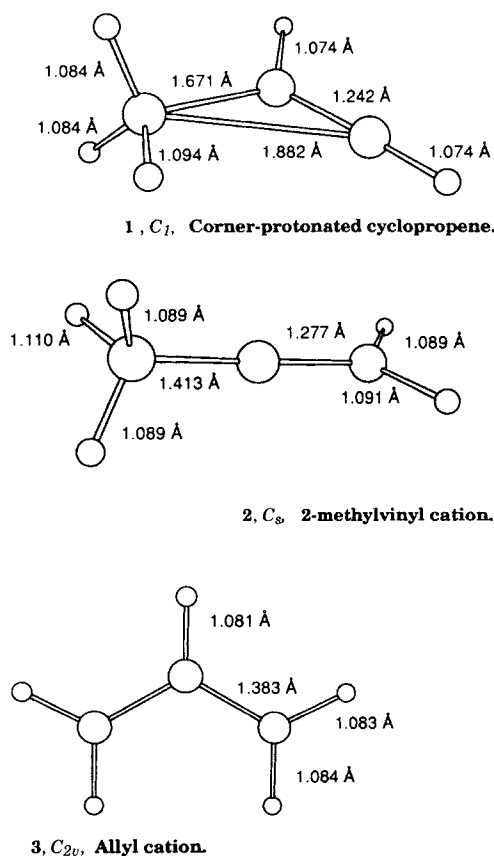


FIGURE 1. MP2-FC/6-31G** intermediates for the reaction $\text{CH}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{H}_2$.

TABLE I.

Total Energies (hartree) and Relative Energies (kilocalories per mole) Using MP2-FC/6-31G** Geometries and ZPVE Calculated at the MP2-FC/6-31G** Level.^a

Species	Total Energy			Relative Energy		
	MP4-FC/6-31G**		ZPVE	MP4-FC/6-31G**		MP4-FC/6-31G** //MP2-FC/6-31G** +ΔZPVE
	MP2-FC/6-31G**	//MP2-FC/6-31G**		MP2-FC/6-31G**	//MP2-FC/6-31G**	
$CH_2H_2 + CH_3^+$	-116.42829	-116.47805	34.7	0.0	0.0	0.0
1	-116.53582	-116.58295	39.5	-67.5	-65.8	-61.0
2	-116.55880	-116.61017	38.4	-81.9	-82.9	-79.2
3	-116.58108	-116.63159	41.5	-95.9	-96.3	-89.5
4	-116.48066	-116.52608	37.1	-32.9	-30.1	-27.7
5	-116.47123	-116.51602	36.6	-26.9	-23.8	-21.9
6	-116.46281	-116.51661	34.8	-21.7	-24.2	-24.1
7	-116.53409	-116.58014	39.0	-66.4	-64.1	-59.8
8	-116.51822	-116.56590	39.2	-56.4	-55.1	-50.6
9	-116.52779	-116.58024	39.1	-62.4	-64.1	-59.7
Cyclopropenyl cation + H_2	-116.52827	-116.57427	33.4	-62.7	-60.4	-61.7
Propargyl cation + H_2	-116.47571	-116.52859	32.1	-29.7	-31.7	-34.3

^aThe total MP2/6-31G** and MP4/6-31G**//MP2/6-31G** energies (hartree) of reactants and products are, respectively, as follows: acetylene, -77.08167, -77.10914; CH_3^+ , -39.34663, -39.36899; cyclopropenyl cation, -115.37061, -115.40971; propargyl cation, -115.31805, -115.36403; H_2 , -1.15766, -1.16456.

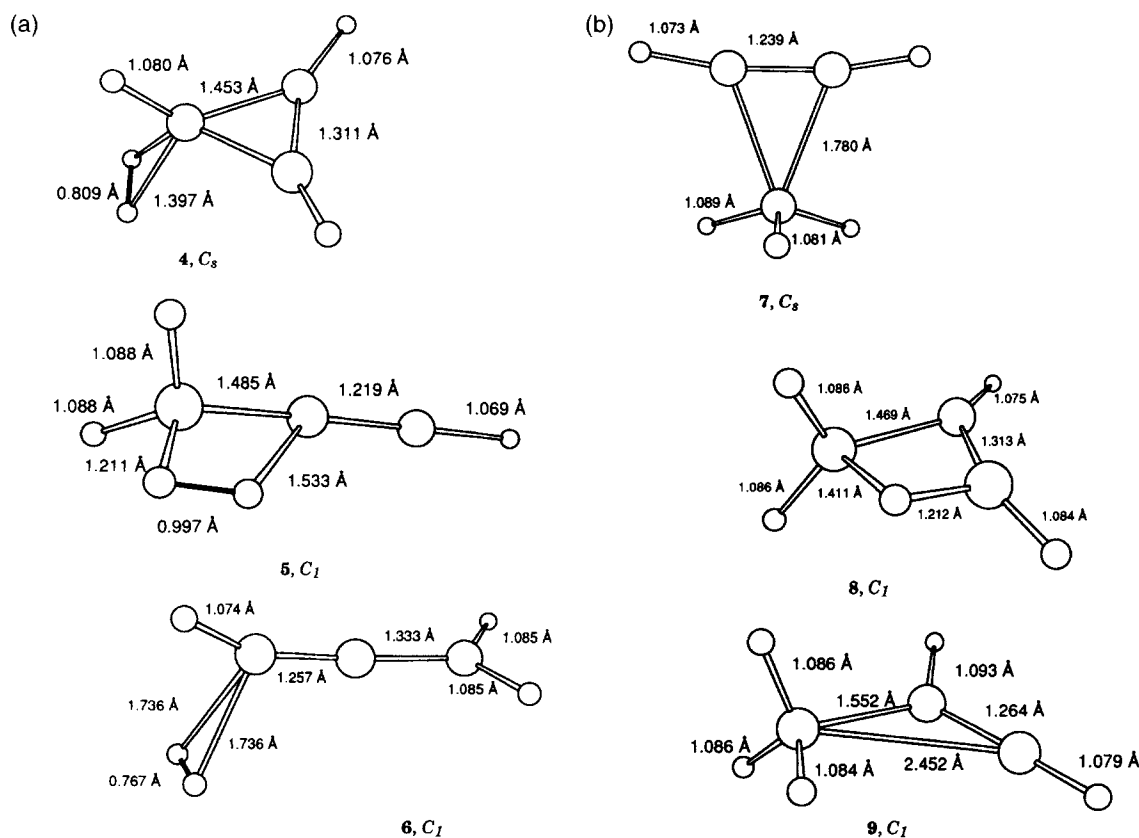


FIGURE 2. MP2-FC/6-31G** optimized transition structures for the H_2 loss: $C_3H_5^+ \rightarrow C_3H_3^+ + H_2$. Structure 7 is for the degenerate isomerization of 1, 8 for the $1 \leftrightarrow 3$ interconversion, and 9 for $1 \leftrightarrow 2$.

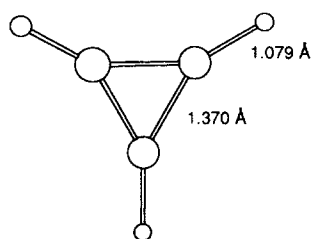
FU/6-31G* theory level. The transition state 7 between the two symmetrical corner-protonated cyclopropenes involves methyl rotations and a low (1.2 kcal/mol) barrier.

Transition structure 4 (see Figure 2) leads corner-protonated cyclopropene 1 to the cyclopropenyl cation, (see Figure 3), and H_2 .¹⁴ In 4 the two H atoms separated by 0.809 Å lead to the H_2 molecule. This is the lowest energy transition structure giving $C_3H_3^+ + H_2$ products. Transition structures 5 and 6 (see Figure 2) are open-chain structures leading from the 2-methylvinyl cation (2) to the propargyl cation (see Figure 3) and H_2 . In 5 the hydrogen molecule forms from one H atom of the CH_3^+ moiety and one H atom of a CH group; note the 0.997 Å separation in Figure 2. In transition structure 6 the hydrogen molecule is formed from two H atoms of the CH_3^+ moiety with a 0.767 Å separation (see Figure 2). Transition structure 6 is 2.2 kcal/mol lower in energy than transition structure 5 at MP4-FC/6-31G**//MP2-FC/6-31G** + ZPVE (see Table I).

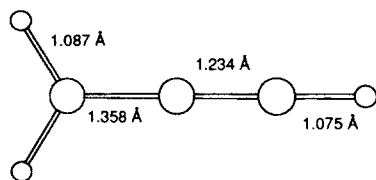
The formation of the cyclopropenyl cation + H_2 (−61.7 kcal/mol) as well as the formation of propargyl cation + H_2 (−34.3 kcal/mol) are both exoergic processes, although the cyclopropenyl cation is 27.4 kcal/mol more stable than the

propargyl cation at the MP4-FC/6-31G**//MP2-FC/6-31G** + ZPVE level. The exoergicity corresponding to the formation of cyclopropenyl cation + H_2 (−61.7 kcal/mol) agrees quite well with the latest ΔH values reported in experimental studies (61.1 kcal/mol).^{6d}

Our calculations indicate that both cyclopropenyl and propargyl cations are generated in the $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$ fragmentation since $C_3H_5^+$ complexes evolve through transition structures 4, 5, and 6 to give $C_3H_3^+$. IRC calculations confirm that structure 4 links the corner-protonated cyclopropene (1) to the cyclopropenyl cation + H_2 , and structures 5 and 6 link the 2-methylvinyl cation (2) to the propargyl cation + H_2 . For the attack of CH_3^+ on acetylene, we assume that, at the lower energies, complete deuterium scrambling takes place via the allyl cation degenerate isomerization.^{8f} Corner-protonated cyclopropene (1) easily gains access to this mechanism through transition structure 8. Product formation from scrambled $C_3H_2D_3^+$ intermediates through transition structures 4, 5, and 6 would give $C_3H_2D^+$ and $C_3HD_2^+$ in the proportions 1:2, in agreement with experimental findings.^{6b,e} In contrast, at the higher energies, where the intermediate complex lifetime is reduced, we may assume that complete deuterium scrambling does not occur owing to the competition with H_2 loss processes. Then, product formation can take place through transition structures 4, 5, and 6 either from unscrambled $C_3H_2D_3^+$ intermediates giving $C_3H_2D^+$ and $C_3HD_2^+$ in the 2:1 ratio or from scrambled intermediates giving $C_3H_2D^+$ and $C_3HD_2^+$ in the proportions 1:2. Thus as the energy of the system increases, the $C_3H_2D^+$ and $C_3HD_2^+$ proportions would tend to be about 1:1 in agreement with experiment.^{6e}



Cyclopropenyl cation, D_{3h} .



Propargyl cation, C_{2v} .

FIGURE 3. MP2-FC/6-31G** products for the reaction $CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2$.

Conclusion

The formation of $C_3H_3^+$ from the reaction of CH_3^+ with acetylene takes place via $C_3H_5^+$ intermediates through three alternative transition structures more stable than reactants, leading one of the intermediates to the cyclopropenyl cation and the other two to the propargyl cation. The composite nature of the metastable peak for the $[C_3H_5]^+ \rightarrow [C_3H_3]^+ + H_2$ fragmentation is theoretically rationalized by the reaction channels determined by these transition structures. The proportions of deuterated products obtained experimentally when CD_3^+ reacts with acetylene are explained by assuming that at lower energies complete deuterium

scrambling takes place so that the subsequent loss of H_2 , D_2 , and HD statistically gives $C_3H_2D^+$ and $C_3HD_2^+$ in the 1:2 ratio. At higher energies, where the intermediate complex lifetime is reduced, formation of products from unscrambled $C_3H_2D_3^+$ intermediates competes with the scrambling process rendering a 1:1 proportion of $C_3H_2D^+$ and $C_3HD_2^+$.

Acknowledgments

The work at Erlangen was supported by the Fonds der Chemischen Industrie and the Convex Computer Corporation.

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